

Nature of Charge Carriers and Origin of “Colossal” Magnetoresistance in Perovskite Manganite

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Using electron energy-loss spectroscopy (EELS) measurements in NCEM’s recently installed FEG/TEM, researchers have conclusively shown that the charge carriers responsible for the conduction mechanism in manganites have significant O_{2p} hole character. This discovery proves that these manganites are insulators of the charge-transfer rather than the Mott-Hubbard type, questions the validity of the well established “double-exchange” model of magnetoresistance and explains the origin of CMR. Based on the publication of these results, a first new rigorous theoretical formulation to explain CMR and metal-insulator transition has been proposed by a Russian research group..

Background - Perovskite manganites, which have the general formula $R_{1-x}A_xMnO_3$ ($R = La, Pr, \text{ or } Nd$ and $A = Ca, Sr, Ba, \text{ or } Pb$), have generated much recent interest because they exhibit “colossal magnetoresistance” (CMR), i.e. a small change in an applied magnetic field dramatically changes the electrical resistance of the material. Materials that exhibit this effect are being developed for various field-sensing applications but currently, the mechanism by which CMR occurs is not known.

A starting point is to understand the basic conduction mechanism in manganite materials. Conduction in these materials is explained by the “double exchange” mechanism, where the conductivity is attributed to electrons hopping back and forth between neighboring manganese ions. Such hopping is a maximum when the magnetic moments of the manganese ions are aligned parallel and a minimum when they are aligned antiparallel. In short, these materials show metallic conductivity when they are ferromagnetic and insulating behavior when they are antiferromagnetic. Moreover, they change from metallic to insulating behavior as a function of temperature. Such a transition can be accomplished either by a transfer of electron between manganese levels (Mott-Hubbard type) or from oxygen to manganese levels (charge-transfer type). The double exchange model inherently assumes a Mott-Hubbard type insulator.

Accomplishment - The NCEM team investigated the conduction mechanism by preparing a range of well-characterized samples by the sol-gel method [1]. By carefully doping they controlled the divalent ion content in one set of samples and in another set of samples, the oxygen content was varied by systematic annealing [2].

The resistivity of these samples, measured as a function of temperature (figure 1a), ranges from insulating to metallic, with some intermediate compositions showing metal-insulator transitions. The electronic structure of these well characterized samples was measured by electron energy-loss spectroscopy using the newly installed CM200 microscope at the NCEM. The intensity of the O-K edge (figure 1b), which is a measure of the density of holes on oxygen sites, shows a systematic variation not with the divalent content, but with the resistivity of the films. Similar results were also obtained for a fixed divalent content but with varying oxygen doping. This shows that these materials have significant conductivity due to holes on oxygen sites.

These results and their detailed analysis, presented in our recent publication [3] show that the conductivity in these materials is hole-driven and that these holes, having predominantly O_{2p} hole character, contribute significantly to the conduction mechanism, including magnetoresistance, in these materials.

We also present a model of the band evolution that provides new insight into the transport mechanism in these oxides and suggest that the double exchange mechanism, which implicitly

assumes a Mott-Hubbard insulator, has to be revised to include the role of oxygen hole mobility in the conductivity mechanism.

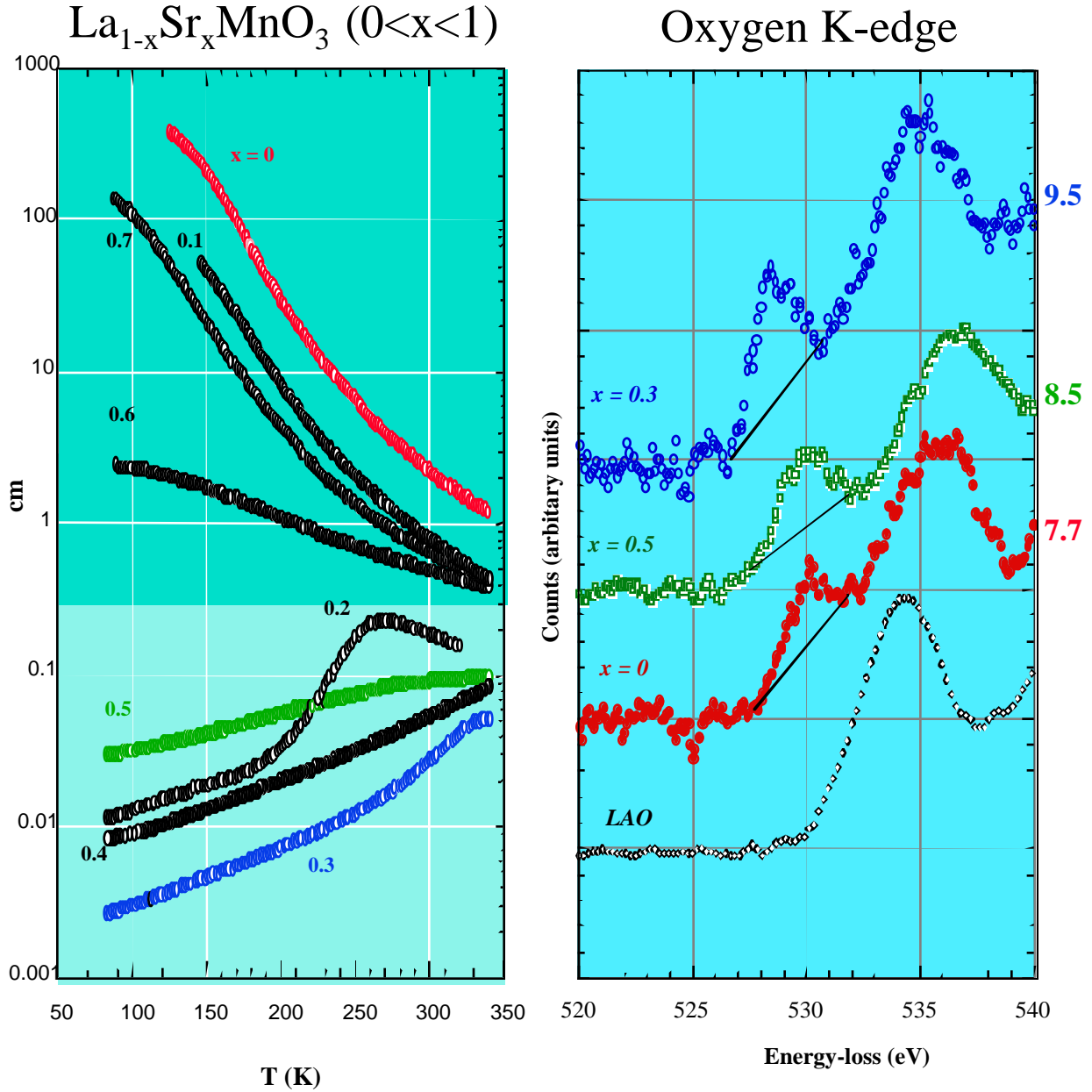


Fig. 1. (a) Temperature dependence of the resistivity of the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films in the composition range $0 < x < 0.7$. (b) oxygen K-edge spectra of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0, 0.3, 0.5$) and LaAlO_3 . The small shifts in the energies of the peaks is due to drift in the high voltage offsets

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